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Fractal kinetic characteristics for dissolving and leaching processes of strontium residue

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Abstract The pore structural characteristics of strontium residue were studied with the N_2 adsorption method (ASAP2010). The kinetic properties concerning dissolving and leaching strontium waste were described by determining the concentrations of Sr^{2+}, Ba^{2+} and soluble sulphides in solutions. The results showed that the specific surface area and pore volume increased with decreasing granule diameter, and the micropore surface of the residue was fractal. In the dissolving and leaching processes of strontium residue, soluble ion concentrations increased with decreasing granule diameter of the residue, and the reaction dimension was lower than the fractal dimension of pore surface. Sr^{2+} and soluble sulphide concentrations significantly exceeded the defined standard values, while Ba^{2+} concentrations did not, either in the dissolving or leaching solutions. In addition, dissolving and leaching reactions selectively occurred on the micropore surface of strontium residue.

Key words strontium residue; surface fractal dimension; dissolving; leaching, reaction dimension

1 Introduction

Strontium carbonate is manufactured with several methods, including carbon reduction, metathetical reaction, pyrolysis of strontianite and torrefaction, etc. The metathetical reaction method is hardly to be conducted in industrial plants in China because of its low reaction rate, long process circuit, low yield and difficulties in disposal of sodium or ammonium ions in wastewater. The application on the pyrolysis method of strontianite was restricted due to the lack of raw materials. Under the condition that a wide range of ore grades, less raw materials being able to be used with short procedures, the carbon reduction method (CRM) has been adopted popularly in the world (Chen Yingjun, 2002; Zhang Qingli et al., 2005; Zhang Jin and Liao Jialin, 1992). The method was performed by mixing celestite and coal in an appropriate proportion. $SrSO_4$ in celestite was deoxidized into SrS when those materials were heated at a high temperature (1150℃), and then SrS was hydrolyzed and solid $Sr(OH)_2$ was formed. The filtrate reacted with CO_2, Na_2CO_3 or NH_4HCO_3 after several times of impurity extraction, and $SrCO_3$ was deposited. Ultra-pure strontium carbonate could be further prepared by adding chloride solution, nitrate solution or alkali separation agents.

Strontium residue is a kind of solid waste from strontium carbonate industry. The waste is mainly involved in extracting process and contains raw materials of non-reaction (e.g. ore and coal) (Mao Qingeng, 1990; Liang Kaiyu et al., 2001). There is 2.5-ton extracting strontium waste in the production of every 1.0-ton strontium carbonate. It is noticed that a great amount of land was occupied by the solid waste, and its leaching solution would result in serious environmental pollution. The problem is difficult to solve because of the high level of contamination. Although some studies on the improvement process of producing strontium carbonate were reported, few studies have focused on the environmental issue and comprehensive utilization of strontium tailings (e.g. strontium gangue and residue) in recent years (Zhang Qingli et al., 2005; Xu Longjun et al., 2008 a, b). Barbara Nisi et al. (2006) thought that the Sr isotopic composition of the Arno River Basin waters is affected by a complex mixing process to which, at least, five components (carbonatic, silicatic and Ca-SO_4^- rich evaporitic lithologies and thermal and sea waters) make contributions. The purpose of our study is to explore the way of solving the problem of pollution and promoting the best utilization of strontium waste. Thus, it is important to investigate the pore structure characteristics of strontium residue and the kinetics of the dissolving and the leaching process with experiments.

2 Materials and methods

2.1 Main instruments and reagents

Instruments include the instrument for analyzing specific surface area and pore diameter (ASAP2010, USA), electronic balance (FA1004N, Jingke Electronic Balance Factory, Shanghai, the accuracy is 0.0001 g), reciprocating level oscillator (Xinhang Instrument Factory, Zhejiang, China), and valve electric stove (SK2-6-12, Experiment Electric Stove Factory, Shanghai, China).

Reagents include anhydrous sodium carbonate, EDTA, boracic acid, potassium dichromate, acetic acid, zinc powder, potassium iodinate, iodine, soluble maizena, ammonium acetate, naphthol green B, Thiazole Yellow, Eriochrome black T, aqueous ammonia, ammonium chlorinate, sodium thiosulfate pentahydrate, magnesium sulphate, and zinc acetate (AR).

Strontium waste residue was provided by the factory producing strontium carbonate in Tongliang, Chongqing. The chemical components of the strontium residue are listed in Table 1 (Qu Ge, 2008).

Table 1. The chemical components of strontium residue

Component	Sr	SiO_2	Fe	Al	Ba
Content (%)	26.49	9.64	1.36	5.52	0.29

The strontium residue was separated with sample sieves after air drying. Five samples measuring at -20–60, -60–80, -80–120, -120–200 and -200 meshes were prepared to determine the pore structure, corresponding to the average diameters of 0.540, 0.215, 0.150, 0.0975 and 0.054 mm, respectively (Qu Ge, 2008). The samples, as fine as -40–60, -60–80, -80–200 and -200 meshes (namely the average diameters are 0.335, 0.215, 0.130 and 0.054 mm, respectively) , were collected for dissolving and leaching tests.

2.2 Experimental methods

2.2.1 Pore structural characteristics of strontium residue

Nitrogen adsorption isotherm of strontium residue at 77.23 K was measured with the instrument for measuring specific surface area and pore diameter (ASAP2010). The pore volume distribution and pore specific surface area of the samples were calculated with BJH model.

2.2.2 Dissolving test of strontium residue

The influence of strontium residue on the environment was investigated by measuring the concentrations of soluble strontium (Sr^{2+}), barium (Ba^{2+}) and sulfides (S^{2-}, SO_3^{2-} and $S_2O_3^{2-}$). The process was simply called the dissolving test. In this way, the dissolving process was distinguished from the leaching process. The mixture of 0.5000 g of strontium residue sample and 3 g of flux（Na_2CO_3:K_2CO_3:H_3BO_3=2:1:1）was heated to 800℃ in a muffle furnace for 20 minutes, and then it was put into water in a flask. After filtration, the sediment was washed with 1% Na_2CO_3 solution, and was resolved with 1:2 heat hydrochloric acid and diluted to 250 mL as the test solution. The concentrations of soluble strontium and barium in the test solution were measured with the improved EDTA-potassium dichromate-iodimetry (Qu Ge, 2008; Yang Yi, 1998)。

The concentrations of soluble sulfides were determined with iodometric method (Qu Ge, 2008; Yang Xinbin et al., 2000). Fifteen grams of sample in the beaker was dissolved in water, filtrated, and diluted to 500 mL as the test solution.

2.2.3 Leaching test of strontium residue

The static leaching experiments on strontium residue were performed in the light of discrimination standard on hazardous waste (GB5085.3-2007). 100.0 g of strontium residue was put into a 2.0-L flask, and leached with 1.0 L of distilled water (pH=7.02). The leaching flask was fixed in a reciprocating level oscillator, controlling the surge frequency at 110±10 r/min, and reacted for 8 hours at room temperature. The reacting solution was filtrated with intermediate speed quantitative filter paper after the solution was statically placed for 16 hours. All filtrate (leaching solution) was collected. For the determination of Sr^{2+}, Ba^{2+} and soluble sulphide concentrations, please refer to the literature (Qu Ge, 2008; Yang Yi, 1998; Yang Xinbin et al., 2000).

3 Results and discussion

3.1 The effect of average diameter on the pore structure of strontium residue

Classification of pore sizes issued by International Union of Pure and Applied Chemistry (IUPAC) has been applied in the chemical field. The pores in strontium residue could be classified as micropore (< 8 nm), interim pore (8–100 nm) and macropore (> 100 nm) according to the coal's pore classifying scheme-based industrial adsorbents (Xu Longjun et al., 2004). The distribution of strontium residues on the special surface is given in Table 2.

Table 2. The special pore surface areas of strontium residues (the data were acquired with BJH model) (m^2/g)

Average diameter (mm)	Macropore A_1	A_1/A_T (×100%)	Interim pore A_2	A_2/A_T (×100%)	Micropore A_3	A_3/A_T (×100%)	Total pore special surface area A_T
0.540	0.127	0.113	11.28	10.06	100.7	89.74	112.2
0.215	0.063	0.048	10.21	7.81	120.5	92.14	130.8
0.150	0.075	0.054	15.55	8.55	165.9	91.41	181.4
0.0975	0.096	0.047	14.54	7.09	190.3	92.86	204.9
0.054	0.102	0.063	15.80	7.10	203.5	91.50	222.4

Table 3. The pore volumes' distributions of strontium residue (BJH model) ($10^{-3}cm^3/g$)

Average diameter (mm)	Macropore V_1	V_1/V_T (×100%)	Interim pore V_2	V_2/V_T (×100%)	Micropore V_3	V_3/V_T (×100%)	Total pore volume V_T
0.540	4.09	2.92	46.27	33.07	89.55	64.00	139.9
0.215	2.21	1.30	60.92	35.92	106.4	62.77	169.6
0.150	2.78	1.15	93.17	38.54	145.8	60.31	241.7
0.0975	3.87	1.54	83.21	33.26	163.1	65.19	250.2
0.054	3.42	1.18	111.7	38.41	175.7	60.42	290.8

As can be seen in Table 2, the total special surface area increases with decreasing granule size of strontium residue. The result was in accordance with the properties of general porous matter. The special surface areas of micropore, interim pore, and macropore in the residue account for 90%, about 10%–15%, and 0.047%–0.113% of the total special surface area, respectively. It is indicated that micropores grew well and were dominated in strontium residue.

Pore volume distribution of strontium residue was provided in Table 3. It was found from the table that the volume fractions of micropore and interim pore constituted over 97% of the total volume, moreover that of micropore constituted over 60% of the total volume. It could be deduced that strontium residue had high activity including adsorption and dissolving abilities. In addition, the total pore volume increased with decreasing granule diameters of strontium residue.

It is known that the surface of most materials is fractal at the molecular level. If the surface of a grain is fractal, the relationship between surface area and particle's radius is described as follows (Fairbridge et al., 1986; Pfeifer and Avnir, 1983; Avnir et al., 1983):

$$A \propto R^{D-3} \tag{1}$$

where A is the surface area, R is the particle radius, and D is the surface fractal dimension. The data in Table 2 are fitted with Equation (1). D is equal to 2.68, and the correlative coefficient is -0.955. The result suggests that the micropore surface of strontium residue displays fractal characteristics. The pore of anomalistic shape is beneficial to surface reactions.

3.2 Effect of strontium residue diameter on the contents of soluble species

The contents of soluble strontium, barium and sulfides could be described as their concentrations in test solution for strontium residues of different diameters. The concentrations of components in the solution are listed in Table 4.

Table 4. Concentrations of soluble components in the dissolving test of strontium residue (mg/L)

Diameter (mm)	0.335	0.215	0.13	0.054
$C_{\mathrm{Sr}^{2+}}$	525.7	546.9	569.4	597.3
$C_{\mathrm{Ba}^{2+}}$	0.83	0.89	0.98	1.01
$C_{\mathrm{S_2O_3^{2-}}}$	96.75	106.3	113.6	125.9
$C_{\mathrm{SO_3^{2-}}}$	29.25	30.98	35.36	46.82
$C_{\mathrm{S^{2-}}}$	40.50	46.89	47.56	56.32

It is noticed from Table 4 that the concentrations of soluble strontium, barium and sulfides in the test solution rise with the drop of granule diameter of strontium residue. In view of "Wastewater Integrated Discharge Standard" (GB8978-1996), the first class discharge standard of sulfides in wastewater is 1.0 mg/L. Referring to "Discharge standard of pollutants in strontium compounds industry" (DB 50/247-2007), the discharge limit of strontium is 10.0 mg/L, and that of barium is 2.0 mg/L. Thus, the concentrations of strontium and sulfides in the test solution greatly exceed the relevant discharge limits, but those of barium do. The soil and surface water would be seriously polluted if the percolation prevention and disposal of leaching solution were not reasonably completed.

3.3 Effect of strontium residue diameter on ion concentrations in the leaching solution

The ion concentrations in the leaching test are listed in Table 5 for strontium residues of different diameters.

As is seen in Table 5, it is shown that the concentrations of strontium, barium and sulfides in the leaching solution increase with decreasing diameter of strontium residue. Moreover, both strontium and sulfide concentrations are significantly higher than the discharge limits, and those of barium are not.

Table 5. Ion concentrations in the leaching solution from strontium residue (mg/L)

Diameter (mm)	0.335	0.215	0.13	0.054
$C_{\mathrm{Sr}^{2+}}$	634.37	663.25	689.8	711.47
$C_{\mathrm{Ba}^{2+}}$	1.23	1.29	1.31	1.40
$C_{\mathrm{S_2O_3^{2-}}}$	275.2	286.23	295.6	302.25
$C_{\mathrm{SO_3^{2-}}}$	29.10	34.62	38.97	40.96
$C_{\mathrm{S}^{2-}}$	23.30	25.68	29.65	32.72

3.4 Fractal kinetics on dissolving and leaching of strontium residue

Our test data in this study indicated that the micropore surface of strontium residue had fractal characteristics. The reaction rate of heterogeneous reaction was relative to the fractal dimension on the reaction surface. In fact, the relationship between the reactivity of the surface and the fractal dimension was studied by many researchers (Farin and Avnir, 1987; Daccord, 1987; Kopelman et al., 1986; Xu Longjun et al., 2008c). Farin and Avnir (1987) thought that diffusion gave rise to differences in experimental features and reaction properties. Namely, the fractal dimension is considered as a controlling geometric parameter. Thus, equation (1) is re-written as follows:

$$S \propto R^{D_R-3} \tag{2}$$

where S is effective surface area, and D_R is effective surface reaction dimension in the reaction.

It was thought that initial rate (v, mol· time^{-1}· g^{-1}) in surface reaction was direct proportional to effective surface area of the reaction (Tkacova and Balaz, 1985),

$$v \propto S \tag{3}$$

Thus, equation (2) could be changed as follows,

$$v \propto R^{D_R-3} \tag{4}$$

Actually, the concentration (C) in dissolving solution or leaching solution are direct proportional to the reaction rate (v).

$$C \propto v \tag{5}$$

Therefore, Equations (6) and (7) could be obtained from Equations (4) and (5).

$$C \propto R^{D_R-3} \tag{6}$$

or

$$C \propto d^{D_R-3} \tag{7}$$

where d is the granule diameter (mm).

Equation (7) is applied to fitting the data in Table 4 and Table 5. The results are listed in Table 6. It is obvious that the dissolving and leaching processes of strontium residues display fractal kinetic characteristics, and surface dimensions are within the range of 2.74–2.96. The average surface dimension is 2.87.

Table 6. Kinetic parameters for the dissolving and leaching processes of strontium residue

Ion		Sr^{2+}	Ba^{2+}	$\mathrm{S_2O_3}^{2-}$	$\mathrm{SO_3}^{2-}$	S^{2-}
Dissolving process	D_R	2.93	2.89	2.86	2.74	2.83
	Correlative coefficient (r)	-0.992	-0.941	-0.990	-0.988	-0.968
Leaching process	D_R	2.94	2.93	2.95	2.82	2.81
	Correlative coefficient (r)	-0.970	-0.987	-0.959	-0.920	-0.979

It was thought that the dissolving and leaching processes of strontium residue were chemical reactions in the fractal surface. The conclusion was in accordance with the idea of Farin and Avnir (1987), who obtained the reaction dimensions of 31 materials (material constituents) and the surface fractal dimensions of 25 materials by using equation (1) to equation (6). Meantime, the reaction dimensions on dissolving and leaching for strontium residue (2.74–2.96) are totally larger than the surface fractal dimension (2.68). It is indicated that the dissolving and leaching reactions maybe selectively occur on the micopore surface. The case is true for the dissolving of Madagascar quartz in 3.66 mol·L^{-1} HF solution (Farin and Avnir, 1987). The reaction dimension (D_R) and surface fractal dimension of dissolving process of Madagascar quartz are 2.14 and 2.0–2.15, respectively.

4 Conclusions

Special surface area and pore volume distributions for strontium residues of different granule diameters were investigated by using the nitrogen adsorption method. The kinetic properties of the dissolving and leaching processes were discussed in terms of chemical analyses.

(1) The special surface area and pore volume increase with decreasing granule diameter of strontium residue. The micropore surface has fractal characteristics, and the fractal dimension of the residue is 2.68.

(2) The ion concentrations of strontium, barium and sulfides in the dissolving and leaching processes increase with decreasing granule diameter of strontium residue. The soluble strontium and sulfide concentrations are extremely higher than the relevant

discharge limits, but the barium concentrations are not. The unreasonable preventing percolation and the collection of leaching solutions caused serious pollution of surface water and soil.

(3) The reactive dimensions on the dissolving and leaching processes are higher than the surface fractal dimension of strontium residue. The reactive process is a heterogeneous chemical reaction on the fractal surface. The dissolving and leaching reactions selectively happen on the micropore surface of strontium residue.

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